NASA TN D-106

TN-27
195549
31P.

TECHNICAL NOTE
D-106

INVESTIGATION OF ALUMINUM PHOSPHATE COATINGS FOR THERMAL INSULATION OF AIRFRAMES

By A. G. Eubanks and D. G. Moore

National Bureau of Standards

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON November 1959

(NASA-TN-D-106) INVESTIGATION OF ALUMINUM PHOSPHATE COATINGS FOR THERMAL INSULATION OF AIRFRAMES (National Bureau of Standards) 31 p

N89-70612

Unclas
00/27 0195549

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

TECHNICAL NOTE D-106

INVESTIGATION OF ALUMINUM PHOSPHATE COATINGS FOR THERMAL INSULATION OF AIRFRAMES

By A. G. Eubanks and D. G. Moore

SUMMARY

Coatings bonded with aluminum phosphate were investigated for possible use as thermal insulation on airframes. The coatings were prepared by mixing inert ceramic fillers with an aqueous solution of monoaluminum phosphate; they were applied at thicknesses from 0.002 to 0.20 inch to various metals and alloys by spraying, brushing, or dipping. The heavier applications were reinforced with expanded SAE 1020 carbon steel spot-welded to the base metal. The coatings became permanently hard and insoluble in water when cured for 2 hours at 400° F or for 1/2 hour at 600° F.

Measurements showed the following range in properties for various compositions: (1) Hardness, 2.5 to 4 on Moh's scale; (2) density, 1.4 to 2.4 g/cm^3; (3) refractoriness, 2,810° to 3,170° F by cone-fusion test; (4) thermal conductivity, 5 to 10 $Btu/ft^2\text{-}hr(^\circ F/in.)$; (5) thermal-shock resistance on stainless steel, poor to excellent depending on coating thickness; and (6) total hemispherical emittance, 0.5 to 0.7 at 1,500° F on initial heating depending on coating composition.

The combination of high refractoriness, low curing temperature, and variable emittance (depending on composition) suggests that the coatings, when applied as a thin layer, might be useful in regulating heat transfer by radiation. Heavy insulating layers were sensitive to thermal shock and hence would be unsuited for airframe applications involving rapid temperature change.

INTRODUCTION

The high speeds of present-day missiles and aircraft both within the earth's atmosphere and upon reentry have created serious aerodynamic heating problems. Blunting of the leading edge so that the shock wave would form ahead of the surface and dissipate heat to the air was a major step forward (ref. 1). Even with this design improvement the surface may, in some

instances, reach such high temperatures as to reduce the structural strength of the airframe dangerously.

In applications where such heating occurs, some means must be provided to keep the temperature at or below an acceptable limit. Several methods have been suggested by which excessive temperature "buildup" might be prevented. One is by "sweat cooling" (ref. 1). Another is to circulate liquid coolants beneath the airframe skin. A third method is to apply a coating of suitable thermal properties to critical areas of the outer surface, and thus protect the metal from rapid temperature change, or from excessive temperature in those applications in which the heating is for short durations.

A coating might serve either of two functions in reducing the surface temperature of the metal. First, if its emittance is high, even a thin application could bring about cooler operation by radiating away part of the absorbed heat; second, a thick coating of low thermal conductivity could retard the flow of heat to the metal. For either use, the coating should be light in weight, be heat resistant, have excellent thermal-shock resistance, bond tightly to the airframe, and have a surface of such smoothness that it will not impair aerodynamic efficiency. In addition, application of the coating at low temperature should be feasible. This last requirement is of particular importance since it is impracticable in many cases to subject the airframe to a high temperature during the coating process.

Bonding agents that might be used to prepare coatings with low curing temperatures include the silicones, the soluble silicates (e.g., sodium silicate and potassium silicate), the metal phosphates, and the calcium aluminate hydraulic cements. The silicones are unstable at temperatures above the 1,000° to 1,200° F range, and the soluble silicates lack refractoriness. Although the calcium aluminate hydraulic cements harden at room temperature, they cannot be used in premixed coating compositions because the hardening process begins very shortly after the addition of water. The metal phosphates, however, appeared promising. Exploratory work had shown that coatings containing monoaluminum phosphate gave good bonding to metals, and were quite refractory when cured at a temperature as low as 400° F. Because of this promise, a more complete investigation was indicated.

This report gives the results of the investigation. The goal was to learn as much as possible about the preparation and application of coatings of this type and also to determine such properties of the coatings as might be of engineering interest.

The investigation was carried out in the Enameled Metals Section of the National Bureau of Standards with the financial assistance and under the sponsorship of the National Advisory Committee for Aeronautics.

SYMBOLS

A	cross-sectional area
D	diameter of ball, mm
d	diameter of indentation measured with microscope having a filar eyepiece, mm
E	emittance of specimen
k	thermal conductivity
L	load on ball, kg
T_1	temperature of water-cooled shell, $^{\circ}K$
T_2	temperature of specimen surface, $^{\circ}K$
W_2	power input needed to maintain gage length of specimen at a uniform temperature T_2, erg/(sq cm)(sec)
σ	Stefan-Boltzmann constant, 5.672×10^{-5} erg/(sq cm)(sec)$(^{\circ}K^4)$

Subscripts:

b	bar or bar material
c	coating material

PROPERTIES OF MONOALUMINUM PHOSPHATE

Kingery (ref. 2) studied phosphate bonding in refractories and found that only the acid phosphates (those that contain at least one hydrogen ion) contributed any bonding action to the refractory mixtures studied, and that one of the most powerful of these was monoaluminum phosphate $(Al_2O_3 \cdot 3P_2O_5 \cdot 6H_2O)$. He measured many of the rheological properties of this compound, finding, for example, that the viscosity of aqueous solutions increased with concentration and decreased with temperature. From the results of a number of different experiments and from X-ray diffraction studies he showed that all mechanically held water is evolved at approximately 215° F. This is followed by the loss of half of the combined water at a temperature of 460° F. The resulting product is amorphous,

having the composition $Al_2O_3 \cdot 3P_2O_5 \cdot 3H_2O$. As the temperature is increased above 600° F, some crystallization is observed; at 930° F, the remaining water disappears and the anhydrous aluminum metaphosphate $Al_2O_3 \cdot 3P_2O_5$ is formed.

MATERIALS

The coatings studied in this investigation were composed of an inert filler material bonded with aluminum phosphate. They were prepared by mixing the filler material in powder form with aqueous solutions of monoaluminum phosphate.

The monoaluminum phosphate solution was prepared as follows: Hydrated alumina was ball-milled dry until it passed a U. S. Standard 325 mesh sieve. One hundred and fifty grams of this material were placed in a 1-gallon ball mill with 700 grams of 85 percent orthophosphoric acid and milled for 1 hour. At the end of this time, an additional 150 grams of hydrated alumina were added to the charge. After a second milling period of 2 hours, 750 grams of water were added, and the milling was continued for 15 minutes more. The solution was removed from the mill and allowed to stand for 24 hours. The clear solution was then decanted. The pH of the decanted solution was 1.67 and its specific gravity was 1.344. Calculations based on the weight of unreacted alumina showed that the mol ratio of Al_2O_3 to P_2O_5 in the reaction product was 1.1 to 3. The addition of the 750 grams of water to the mill was necessary to obtain a 40 percent by weight solution since solutions containing more than this amount of monoaluminum phosphate were found to be unstable during storage.

The solution as prepared above attacked aluminum and its alloys rather vigorously and even AISI type 321 stainless steel to a limited extent. It was found that this attack could be prevented by the addition of 12 grams of chromium trioxide (CrO_3) per 100 milliliters of solution and, hence, this amount was added to all monoaluminum phosphate solutions prepared.

A number of possible filler materials were investigated. It was found that almost any material that was inert to attack by acids could be used as a filler. It was also found that small amounts of a reactable impurity seriously reduced the bonding power of the solution. A number of usable filler materials are listed in table 1.

The alloy used in preparing test specimens for evaluating coating properties was AISI type 321 stainless steel. However, a few tests made with 2S-0 aluminum alloy, SAE 1020 carbon steel, and Inconel (80 Ni-15 Cr-5Fe) showed that the coatings could be applied to all of these alloys.

PREPARATION OF COATINGS AND METAL SURFACE

The coatings were prepared by mixing the batch materials for 1/2 hour in a 1-quart ball mill. In each case, the amount of liquid (phosphate solution plus water) added to the filler was sufficient to give a creamy suspension, or slip, when the mixture was removed from the mill. Tests with powdered quartz as a filler (see section on hardness) were used to establish a suitable ratio of phosphate solution to filler. Table 1 lists the coating compositions that were selected for study.

Two methods of preparing the metal surface were investigated. One was simply to clean the surface with an organic solvent. The other was to sandblast. Adherence was somewhat better when the metal surface was prepared by sandblasting.

APPLICATION TECHNIQUES

The application techniques investigated were dipping, spraying, and brushing. All three techniques were found to be satisfactory for applications of 0.005-inch thickness or less. When the coatings were brushed on, however, the brush marks did not smooth out as well as they do with some organic enamels.

For heavier applications the only satisfactory method among those tried was spraying. It was found that the thickness could be built up to as much as 3/8 inch by a series of spray applications separated by short drying periods.

The surface finish of the cured coatings depended somewhat on the fineness of the filler material used. No quantitative measurements were made, but examination under a low-powered binocular microscope indicated that the finishes of the various coatings ranged from what might be obtained on a steel surface by polishing with a number 4/0 emery paper to that obtained with a number 0 emery paper. None of the coatings had a glossy finish.

A smoother surface could be achieved by polishing with fine abrasive paper, but, because of the pore structure of the coating, a high mirror polish could not be obtained.

USE OF REINFORCING MATERIALS

Although it is possible to build up rather heavy layers by the spraying technique, preliminary tests indicated that the heavier

applications were quite sensitive to thermal shock. A recent report by Sklarew, Hauck, and Levy (ref. 3) on the development of thermally insulating coatings for ram-jet applications has indicated that a metal mesh reinforcement will improve the structural stability and thermal-shock resistance of a ceramic insulating layer. After experimenting with a large variety of reinforcing materials, these investigators concluded that expanded metal gave the best performance. This material provides an excellent mechanical interlock because the sides of the mesh are not vertical but are inclined at an angle, thus forming an overhang of metal over each of the mesh openings.

The expanded metal selected for the present investigation was fabricated of 22-gage SAE 1020 carbon steel and had diamond-shaped openings that were approximately 3/16 inch across the shortest dimension and 3/8 inch across the longest. The overall thickness of the material was 0.065 inch and its weight was 0.45 pound per square foot.

Squares of the expanded metal were spot-welded to blanks of type 321 stainless steel, the spot-welds being made at points 1/2 inch apart in each direction. The composite specimens were then sandblasted. Batches of coatings IC-109F, IC-126, IC-115M, and IC-135 were prepared in which the water content was reduced in order to obtain a trowelable mixture. A number of specimens were prepared from each coating. The thickness of the coatings after curing was approximately 0.20 inch.

PROPERTIES OF COATINGS

Because of the number of coating compositions prepared, it was impracticable to carry out all property determinations on each of the coatings. Therefore, a number of representative coatings were selected upon which to make measurements. The properties determined were: (1) Hardness, (2) moisture resistance, (3) thermal-shock resistance, (4) thermal conductivity, (5) refractoriness, (6) thermal expansion, (7) density and porosity, (8) oxidation protection, and (9) total hemispherical emittance.

Hardness

Hardness measurements were made with a model 4JS Rockwell Superficial Hardness Tester on coatings that had been cured at 400° F for 2 hours. The measurements were made with a 15-kilogram load using either a 1/16 inch or a 1/8-inch-diameter ball (T-scale or W-scale) depending upon the hardness of the coating. Since no factors are available for converting values obtained with the 15T scale to those obtained with the 15W, comparisons

between coatings were difficult to make. Therefore, a parameter called the "hardness index" was computed by using the Brinell formula:

$$\text{Hardness index} = \frac{L}{\frac{\pi D}{2}\left(D - \sqrt{D^2 - d^2}\right)}$$

The hardness test results as given in table 1 indicate that the hardness of the coatings is primarily dependent upon the filler used, the harder fillers giving the harder coatings.

Table 1 also includes data on the effect of the amount of the phosphate bonding solution on hardness. Four coatings were prepared by adding various amounts of the phosphate solution and water to a constant amount of powdered quartz (2 percent retained on a U. S. Standard 325-mesh sieve). These coatings are given in table 1 as compositions IC-107, IC-108, IC-109, and IC-110. After the coatings were milled, they were applied by spraying to sandblasted AISI type 321 stainless steel and then air-dried for 1/2 hour. After an additional drying treatment of 1/2 hour at 215° F, three specimens of each coating were cured for 1/2 hour at temperatures of 200°, 400°, 600°, and 800° F. The thickness of the cured coatings was about 0.020 inch. Hardness values were obtained on three specimens of each coating cured at each temperature. Figure 1 is a plot of the hardness index at the four curing temperatures for the four coatings. It is apparent from this plot that hardness, and presumably strength, decreases with a decrease in aluminum phosphate content. The cause is not known for the peak at 600° F in the hardness values for coatings IC-107 and IC-108. If this effect were absent, the curves for these two coatings would probably have the same general shape as those for coatings IC-109 and IC-110, which have lower phosphate contents. The bond-to-filler ratio in coating IC-109 gave both fairly high hardness values and good workability; hence, this ratio was selected for all coatings with designation numbers higher than IC-109.

The hardness of the coatings was also determined using Moh's scale with values ranging from 2.5 to 4.

Moisture Resistance

The moisture resistance of the coatings, and the effect of different curing periods and curing temperatures on this property, were determined by two test procedures.

In the first procedure, the thicknesses of three specimens of each coating were measured to the nearest 0.0001 inch at a selected spot, and the specimens were immersed for 3 hours in boiling tap water having a

pH of 7.2. After this treatment thickness measurements were taken again at the same spot as before.

The second measurement of the moisture resistance was made by using the water-dropping apparatus shown in figure 2. In this test, the specimens were subjected to the impingement of water drops falling a distance of 12 inches. The rate of delivery was 140 ± 4 drops (8.2 ± 0.2 milliliters) per minute. The specimens were held at an angle of 45° to the line of fall of the drops.

The specimens were cured at six different temperatures (room temperature, 200°, 300°, 400°, 600°, and 800° F) and for nine different time periods (10, 20, 30, 40, and 50 minutes and 1, 1½, 2, and 2½ hours) and were then tested for moisture resistance. The coatings became moisture resistant as determined by both of the solubility test conditions when they had been cured at a temperature of at least 400° F for at least 1/2 hour. In a 3-hour boiling-water test performed on specimens cured under these conditions, a slight discoloration of the water showed that the chromium trioxide, which had been added to inhibit attack of the metal, had not been completely converted to an insoluble form. This slight solubility did not seem to affect the moisture resistance of the coatings. No discoloration was noted on coatings cured at 400° F for at least 2 hours or at 600° F for at least 1/2 hour.

W
1
3
0

Thermal-Shock Resistance

Two thermal-shock tests were used in the investigation. One consisted of inserting coated AISI type 321 stainless-steel specimens into a hot furnace, allowing them to remain until they had reached furnace temperature, and then removing them from the furnace to cool in air. This procedure was repeated at each test temperature either until the coating flaked from the metal at one or more spots or until 10 cycles had been completed. The coatings subjected to this test were applied at thicknesses of 0.005, 0.020, and 0.20 inch. The specimens with 0.20-inch-thick coatings were reinforced with expanded metal mesh. A fresh set of three specimens of each thickness was tested at each temperature. The temperatures used were 600°, 800°, 1,000°, 1,200°, 1,400°, and 1,800° F.

The second test procedure was the same as the first except that the specimens were quenched in water. The coating thicknesses for this test were 0.0015 and 0.005 inch. The results of the thermal-shock tests are given in table 2.

The coating having the best thermal-shock resistance among those tested in the unreinforced condition was IC-109F. This coating when

applied at a thickness of 0.0015 inch did not fail when quenched 10 times in water from 1,400° F. At a thickness of 0.020 inch it could be air-quenched from 1,200° F without failure.

The poorest thermal-shock resistance was exhibited by the coating containing calcined alumina (IC-123). This coating when applied at a thickness of 0.005 inch failed at 800° F upon air-cooling.

The use of reinforcing improved the thermal-shock resistance of the thicker applications considerably. In every case the coatings remained anchored to the metal after 10 air-quenches from 1,800° F, the highest test temperature used. It was noted in all the reinforced specimens tested, however, that cracking of the coating and separation from the metal began at about 1,200° F.

Thermal Conductivity

The method selected for the measurement of thermal conductivity of the coating materials was a modification of that used by Van Dusen and Shelton (ref. 4). It consists of imposing a temperature gradient axially along two $1\frac{1}{2}$-inch-diameter AISI type 303 stainless-steel bars between which was placed a wafer of the material to be tested. The gradients were computed from temperature measurements made with thermocouples placed in small holes at known points along both bars.

The coating materials to be tested were prepared in the form of disks approximately 3/16 inch thick and of the same diameter as the stainless-steel bars. This was done by casting the coating slip into a mold lined with Teflon. After removal from the mold, the disks were first dried at 200° F, then cured at 400° F for 2 hours, and finally heated to 1,200° F for 15 minutes. The faces of each disk were next ground flat and parallel to within 0.001 inch with number 600 silicon carbide abrasive on a cast iron lap. The contact surfaces of the stainless-steel bars were prepared in the same manner. After insertion of the disk, a steady state was established and the temperature gradients measured. The specimen was then removed, a portion of the coating material was ground away, and the contact surfaces of the bars and the disk were relapped. Gradients were then remeasured. After several measurements of this type, sufficient data were obtained to determine the temperature gradient in the coating material.

A schematic drawing of the apparatus is shown in figure 3 and a photograph, in figure 4. As can be seen from the drawing, the stainless-steel bars, with the specimen in position between them, are placed in a furnace that is filled with diatomaceous earth. The gradient in the Incoloy shell, which is heated by three independent resistance coils, is matched to the gradient in the bars to minimize lateral heat flow. The heating element

used for establishing the temperature gradient along the bar assembly is inserted into a hole machined into the upper end of the top bar. A pressure of 100 psi is applied to the specimen through the bar assembly with a lever-arm mechanism. This pressure was found to be necessary for achievement of reproducible contact resistances.

The thermal conductivity of the coating material cannot be calculated unless that of the bar material is known. The mathematical relationship between the two is

$$k_c = k_b \frac{A_b}{A_c} \frac{(dt/dx)_b}{(dt/dx)_c}$$

where $(dt/dx)_b$ is the temperature gradient in an infinitesimal layer of the bar material at the interface and $(dt/dx)_c$ is that in the coating material.

Measurements were made on three coatings at 350°, 625°, 900°, and 1,155° F and these measurements were converted to thermal conductivity by using the values for AISI type 303 stainless steel reported in reference 5. The resulting data are plotted in figure 5.

The thermal conductivities of the three coatings fell between 5 and 10 $\left(Btu/ft^2\right)(hr)(^\circ F/in.)$. The conductivities of all three decreased with temperature. The diatomaceous earth coating had the lowest thermal conductivity and the coating containing black-color oxide (IC-126), the highest. The rate of change of conductivity with temperature for coating IC-126 is unusually high. This high rate may be caused by structural changes; a color change was noted in the coating material after testing.

Refractoriness

The pyrometric cone equivalence of four selected compositions was determined in accordance with the ASTM standard method for refractory materials (ref. 6). The results were as follows:

Coating	Filler	Pyrometric cone equivalent	Approx. temp. equivalent, °F
IC-109F	Powdered quartz	31-32	3,074
IC-115M	CeO_2 plus powdered quartz	19	2,809
IC-126	Powdered quartz plus black-color oxide	33	3,169
IC-135	Diatomaceous earth plus powdered quartz	29-31	3,040

Thermal Expansion

In order to measure thermal expansions, a dilatometer was constructed in which the length change of the specimen on heating could be measured with an Ames dial gage.

The specimen used with this equipment was a cylinder 1/2 inch long by 1/2 inch in diameter. The specimens were formed by drying the coating material to a paste-like consistency and then pressing the material into a Teflon mold. After drying at 215° for 1 hour, the specimen blank was removed from the mold and cured at 400° F for 2 hours, and the face surfaces were ground flat and parallel to within 0.001 inch on a lap. A hole for a thermocouple was then drilled halfway through the specimen along its longitudinal axis.

In being set up for a test, the specimen was placed on a clay-bonded fused-alumina base plate that rested in slots cut in the wall of an 18-inch-long Alundum tube with a $1\frac{1}{2}$-inch inside diameter. A second tube of the same material, 12 inches long with a 1-inch outside diameter, was placed inside the larger one, the smaller tube resting on an alumina bearing plate which was supported by the specimen. The Ames dial gage, which could be read to 0.001 millimeter, was mounted rigidly on a brass collar that was secured to the top end of the outer tube with set screws. The gage was positioned in such a way that the probe was in contact with a brass cap which was cemented to the top of the smaller inside tube. By this arrangement any length change of the specimen plus differential changes in length of the inner and outer tubes were transmitted to the dial gage. Heating was carried out by inserting the assembly part deep into a vertical tube furnace.

A specimen of fused silica was used for calibrating the equipment. The heating rate was 8° F per minute, the same as for all subsequent tests. Dial gage readings were made during the heating cycle and also as the specimen cooled with the furnace.

After calibration of the apparatus with the fused silica standard, the thermal expansion of a specimen of high-purity nickel was determined. The following table shows the agreement with established values (ref. 7):

Temperature range, °C	Linear expansion coefficient		
	Literature (ref. 7), in./in./°C	Present measurement, in./in./°C	Variation, percent
25 to 300	14.4×10^{-6}	15.0×10^{-6}	4.2
25 to 600	15.5	15.7	1.9
25 to 900	16.3	16.7	2.5

Improved accuracy would have resulted if the measurements had been made under steady-state temperature conditions. However, for the present work greater accuracy was not important, since the shrinkage behavior of the coatings during rapid heating was of almost as much interest as the thermal expansion.

Thermal-expansion data for five coatings are shown in figure 6; data for AISI type 321 stainless steel taken from reference 5 are shown for comparison. In all coatings which contain quartz as a filler a rapid increase in expansion occurs over the temperature range of 1,000° to 1,200° F. This behavior is caused by the increase in volume resulting from the inversion of alpha to beta quartz. The beta quartz has a negative coefficient of thermal expansion and, after it has formed, the coating material upon further heating shows either a contraction or a very small expansion depending upon the other material present. In the case of the IC-123 coating, which contains no quartz, no such rapid change in expansion is noted.

Coating IC-135, which contains diatomaceous earth and powdered quartz as the filler materials, gave a curve somewhat different from those for the other coatings. As in the other coatings, uniform expansion occurred up to the curing temperature of 400° F. Above 400° F, the rate of length change with increasing temperature decreased, probably because of a shrinkage in the coating structure. This shrinkage tendency was apparent in all of the coatings, but only in the one containing diatomaceous earth (IC-135) was it sufficiently great from 500° to 850° F to produce a net contraction.

The expansion data plotted in figure 6 were obtained during the initial heating of the cured specimens to 1,600° F. As would be expected, part of the shrinkage noted on this first heating was not evident in subsequent heatings of the five coatings. Figure 7 shows the difference in expansion occurring during the first and second heatings of coating IC-123. This result is fairly typical.

Density and Porosity

Bulk density and apparent and true porosity were determined by means of ASTM standard procedures for refractory materials (refs. 8 and 9), with the following exceptions: (a) In determining true specific gravity, the material was crushed to pass a U. S. Standard 100-mesh sieve, and (b) the specimens were not so large as specified in the standard, being on the order of 10 grams in weight.

Results of these determinations are given in table 3. The bulk densities of the coatings ranged from 1.422 grams per cubic centimeter for the diatomaceous earth coating (IC-135), which was one of the lightest coatings prepared, to 2.415 grams per cubic centimeter for the cerium oxide coating (IC-115M), which was one of the heaviest. Based on these figures, 100 square feet of the IC-135 coating 0.020 inch thick would weigh 15 pounds.

Oxidation Protection

The oxidation protection provided by coating IC-109F for mild steel was determined as follows: The coating was applied to 10 specimens of SAE 1020 carbon steel of known thickness. The coated specimens, along with 10 bare specimens, were then placed in a resistance-heated furnace at 1,500° F for 20 hours. At the end of this time the oxide layer was removed and thickness measurements were taken. A loss of metal thickness occurred for both groups of specimens, but the decrease observed for the uncoated specimens was about five times as great as that for the coated ones.

Total Hemispherical Emittance

The total hemispherical emittance was measured[1] for three of the coatings using a modification of the hot filament method as described by Worthing (ref. 10). For these measurements the 0.010-by-0.266-by-8-inch specimen strip was heated by internal resistance. The power input required to maintain a short center section of the strip at uniform temperature in vacuum was observed and this value was then converted into terms of the emittance of the specimens through use of the following relationship:

$$E = \frac{W_2}{\sigma\left(T_2^4 - T_1^4\right)}$$

---

[1]The emittance measurements were made by Mr. J. C. Richmond of the NBS staff.

Measurements made on two specimens of oxidized Inconel gave values over the temperature range of 600° F to 1,670° F that agreed almost exactly. The deviation of this determination from values reported in the literature (ref. 11) was about 3 percent.

Emittances were measured on coatings IC-109F, IC-115M, and IC-126 applied to specimen strips of Inconel. The coatings were approximately 0.010 inch thick.

The specimen temperature was measured with a 0.005-inch-diameter base-metal thermocouple formed by separately welding the two wires to the surface of the Inconel specimen. A correction for the temperature drop through the coating was computed from a knowledge of the metal temperature, the rate of heat flow, and the thermal conductivity of the coating material.

W
1
3
0

The measured emittances are plotted as a function of temperature in figure 8. Values obtained for ceramic coating A-418 with the same apparatus are included for comparison.

The coatings tested have nearly the same total hemispherical emittance up to about 1,000° F. At higher temperatures the difference among the coatings becomes greater, coating IC-115M having an emittance of about 0.5 and IC-126, one of about 0.7 at 1,500° F.

The data shown were obtained on the first heating of the specimens above the 400° F curing temperature. On subsequent heatings the emittance-versus-temperature curves of the coatings were displaced upward. The increase in emittance was slight, however, for all of the coatings except IC-126. On the second heating, this coating had a total hemispherical emittance of about 0.9 at 1,300° F. Such a large increase would only be brought about by a change in the material during the first heating.

CONCLUDING REMARKS

A new type of ceramic coating has been described in which ceramic oxide powders are bonded with monoaluminum phosphate. The resulting coatings do not require a high firing temperature; curing at 400° F imparts stability to the structure and provides satisfactory water resistance. A good bond to clean sandblasted metal surfaces was obtained.

The coatings, after curing, are glass free. The surface is hard, but not as hard as flame-sprayed alumina or fired ceramic coatings. Softening temperatures fall in the range of 2,800° to 3,150° F.

The coatings, although porous, provide some oxidation protection for metals like mild steel. The thermal conductivities of the coatings are low, being of the order of one-twentieth that of the 18-8 stainless steels and one five-hundredth that of aluminum alloys at room temperature.

The coatings when applied to stainless steel at thicknesses of 0.20 inch or greater do not withstand repeated thermal shock by air-cooling from temperatures above 1,200° F. Such heavy applications will, however, withstand a single rapid heating to a much higher temperature, and thin layers (0.001 inch to 0.002 inch) will withstand repeated water-quenching from 1,400° F.

The surface texture of the coatings is dependent upon the application technique. Sprayed or dipped coatings are much smoother than layers applied by brushing.

The total hemispherical emittance of the coatings is dependent on the type of filler used and, when the coatings are applied by spraying, ranges from 0.5 to 0.7 at 1,500° F in the initial heating above 400° F. The emittance of most coatings is slightly higher in subsequent heatings than in the initial heating. Coating IC-126 is an exception. When heated to high temperature for the first time this coating apparently undergoes a permanent change which is accompanied by an increase in emittance on subsequent heating to about 0.9 at 1,300° F.

Coatings applied as heavy layers would provide thermal insulation except that such layers when applied at the necessary thickness are susceptible to cracking by thermal shock. Reinforcement with expanded metal imparts mechanical strength to a heavily applied layer; however, the presence of the metal reinforcement lowers the insulation value of the coating and increases its weight. In addition, good surface textures are difficult to achieve; also, shrinkage cracks occur when layers reinforced with expanded metal are heated above 1,200° F.

The authors believe that the greatest promise for the new coatings lies in their potential use as thinly applied layers. Coatings of this type have good thermal-shock resistance when applied at thicknesses of 0.003 inch or less. The coatings could be formulated so as to provide high emittance for airframes. A comparable emittance could of course be achieved on stainless steels and nickel-base alloys by oxidizing the finished airframe at a temperature in the range from 1,600° to 2,000° F. However, such a heat treatment is seldom feasible and the achievement of high emittance through the use of a thin ceramic layer requiring heating to only 400° F might be a more practical approach. The high-emittance skin would permit cooler operation through radiation of thermal energy. In addition, the inherent refractoriness of the coating would permit its

use at much higher temperatures than are possible with coatings that are bonded with organic resins.

National Bureau of Standards,
Washington, D. C., October 15, 1958.

W
1
3
0

REFERENCES

1. Allen, H. Julian, and Eggers, A. J., Jr.: A Study of the Motion and Aerodynamic Heating of Missiles Entering the Earth's Atmosphere at High Supersonic Speeds. NACA TN 4047, 1957.

2. Kingery, W. D.: Fundamental Study of Phosphate Bonding in Refractories, I, Literature Review, II, Cold Setting Properties, Jour. Am. Ceramic Soc., vol. 33, no. 8, Aug., 1950, pp. 239-247.

3. Sklarew, S., Hauck, C. A., and Levy, A. V.: Development and Evaluation of Insulating Type Ceramic Coatings, Part 1, Development and Small Scale Testing. WADC TR 57-577, Aug., 1957.

4. Van Dusen, M. S., and Shelton, S. M.: Apparatus for Measuring Thermal Conductivity of Metals up to 600° C. Jour. Research, Nat'l. Bur. Standards, vol. 12, no. 4, RP 668, 1934, pp. 429-440.

5. Anon.: Metals Handbook. ASM (Cleveland), 1948, p. 556.

6. Anon.: Standard Method of Test for Pyrometric Cone Equivalent (P.C.E.) of Refractory Materials. ASTM Designation: C24-46. Pt. 3 of ASTM Book of Standards. ASTM (Philadelphia), 1955, pp. 711-715.

7. Jordan, L., and Swanger, W. H.: The Properties of Pure Nickel. RP 257, Jour. Res. Nat. Bur. Standards, vol. 5, no. 2, 1930, p. 1291.

8. Apparent Porosity, Water Absorption, Apparent Specific Gravity, and Bulk Density of Burned Refractory Brick. A.S.T.M. Designation: C20-46, A.S.T.M Book of Standards, Part 3, pp. 736-738, 1955.

9. True Specific Gravity of Refractory Materials. A.S.T.M. Designation: C135-47, A.S.T.M. Book of Standards, Part 3, pp. 739-741, 1955.

10. Worthing, A. G.: Temperature Radiation Emissivities and Emittances. Temperature, Its Measurement and Control in Science and Industry, p. 1176. Am. Inst. of Phys., Reinhold Publ. Corp., New York, 1941.

11. O'Sullivan, William J., Jr., and Wade, William R.: Theory and Apparatus for Measurement of Emissivity for Radiative Cooling of Hypersonic Aircraft With Data for Inconel and Inconel X. NACA TN 4121, 1957.

TABLE 1.- BATCH COMPOSITIONS, MILLING TIMES, AND PROPERTIES OF EXPERIMENTAL COATINGS

Ingredient, milling time, or property	Coating																		
	IC-107	IC-108	IC-109	IC-109F	IC-110	IC-112	IC-114	IC-115	IC-115M	IC-119	IC-121	IC-122	IC-123	IC-126	IC-128	IC-129	IC-133	IC-134	IC-135
[a]Aluminum phosphate solution, ml	30	25	20	20	15	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Water, ml	0	0	5	5	10	5	5	5	5	5	5	5	5	5	5	5	5	5	5
[b]Powdered quartz, g	40	40	40	40	40	12.5	-------	-------	20	-------	20	-------	-------	19	19	15	-------	-------	12
[c]Cr_2O_3, g	2.5	2.5	2.5	2.5	2.5	-------	-------	-------	-------	35	-------	-------	-------	-------	-------	30	-------	-------	-------
[d]Al_2O_3, g	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	65	-------	-------	-------	-------	-------	-------
[e]Asbestos, g	-------	-------	-------	-------	-------	25	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
[f]Cerium oxide, g	-------	-------	-------	-------	-------	-------	-------	95	40	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
[g]Color oxide (G221), g	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	38	-------	-------	-------	-------	-------
[h]Color oxide (G621), g	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	38	-------	-------	-------	-------
Diatomaceous earth, g	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	8
[f]Fluorspar, g	-------	-------	-------	-------	-------	-------	40	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
[i]NBS frit 228, g	-------	-------	-------	-------	-------	-------	40	-------	-------	-------	20	40	-------	-------	-------	-------	-------	-------	-------
[j]Powdered mica, g	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	20	-------
Talc, g	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	22	-------	-------
[k]Milling time, min	60	60	60	300	60	20	60	10	10	10	60	60	120	10	10	10	10	10	10
pH	1.2	1.4	1.5	1.8	1.7	-----	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
Rockwell superficial hardness when cured 2 hr at -																			
200° F	15T57.8	15T35.4	15T39.1	-------	15W42.5	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
400° F	15T74.3	15T62.1	15T54.3	15T62.0	15W53.0	15W40.3	15T38.1	15T40.0	15T51.3	15T75.7	15T55.6	15T60.0	15T56.1	15T66.4	15T65.2	15T70.2	15T23.0	15W25.1	15W39.6
600° F	15T82.0	15T75.2	15T57.1	-------	15T32.3	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
800° F	15T78.2	15T64.6	15T49.8	-------	15T32.4	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
[l]Hardness index when cured 2 hr at -																			
200° F	51.3	36.5	36.9	-------	18.3	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
400° F	72.1	52.5	50.0	52.0	23.1	18.6	36.3	37.0	48.3	72.0	50.9	52.0	51.0	60.8	58.8	70.3	25.1	14.8	16.0
600° F	106.7	72.6	51.2	-------	28.4	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------
800° F	78.2	53.1	47.7	-------	28.6	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

[a] Prepared as outlined in section on materials.

[b] 2 percent retained on U. S. Standard 325-mesh sieve.

[c] 3 percent retained on U. S. Standard 325-mesh sieve.

[d] Sized to pass U. S. Standard 60-mesh sieve.

[e] Acid-washed and ball-milled to fine powder.

[f] Sized to pass U. S. Standard 200-mesh sieve.

[g] Cobalt-free black ceramic oxide.

[h] Cobalt-bearing black ceramic oxide.

[i] Porcelain-enamel acid-resistant ground-coat frit sized to pass U. S. Standard 200-mesh sieve.

[j] Heated at 1,200° F for 1 hr.

[k] Milled in 1-qt mill containing porcelain balls.

[l] Hardness index calculated by formula given in text.

TABLE 2.- RESULTS OF THERMAL SHOCK TESTS

Coating	Coating thickness, in.	Quenching medium	Failure, temperature, °F (a)	Cycle number for first failure
IC-109F	0.0015	Water	1600	3
	.005	Water	1400	1
	.005	Air	1600	1
	.020	Air	1400	8
	.20	Air	(b)	-
IC-115M	.0015	Water	1400	1
	.005	Water	1200	1
	.005	Air	1200	1
	.020	Air	1000	1
	.20	Air	(b)	-
IC-126	.0015	Water	1400	1
	.005	Water	1200	1
	.005	Air	1200	1
	.020	Air	1000	8
	.20	Air	(b)	-
IC-123	.005	Air	800	1
	.020	Air	600	4

[a]Temperature at which flaking of coating occurred on one or more specimens.

[b]Coating was held in place by metal mesh after 10 cycles at 1,800° F, the highest test temperature used. Cracking and separation of coating from metal began for all reinforced coatings at 1,200° F.

TABLE 3.- BULK DENSITY, APPARENT POROSITY, AND TRUE POROSITY

Coating	Filler material	Bulk density, g/cc	Apparent porosity, percent	True porosity, percent
IC-109F	Powdered quartz	1.821	25.2	40.4
IC-135	Diatomaceous earth plus powdered quartz	1.422	35.1	53.2
IC-126	Black-color oxide plus powdered quartz	2.040	31.3	38.3
IC-115M	Cerium oxide plus powdered quartz	2.415	33.1	42.6

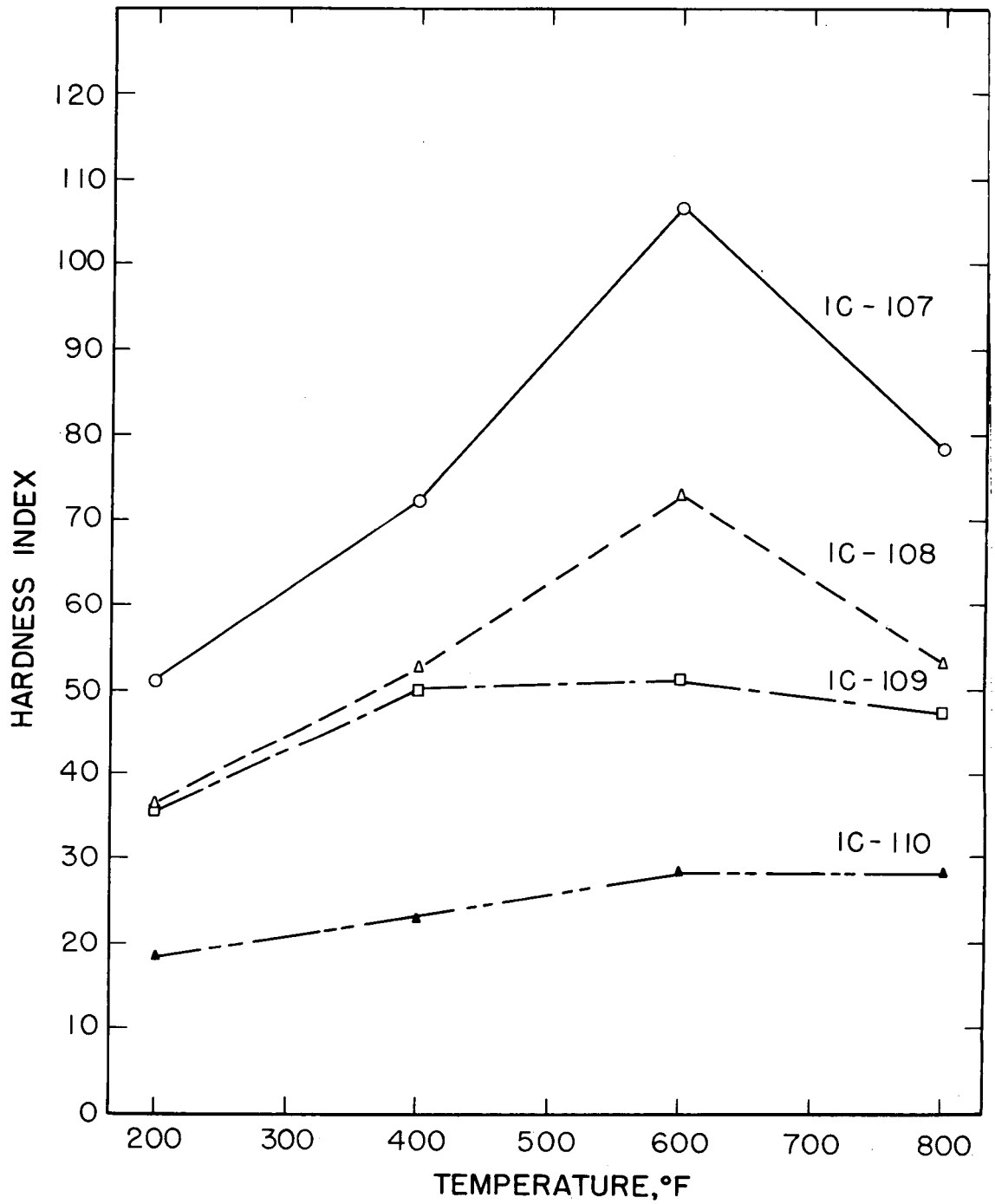
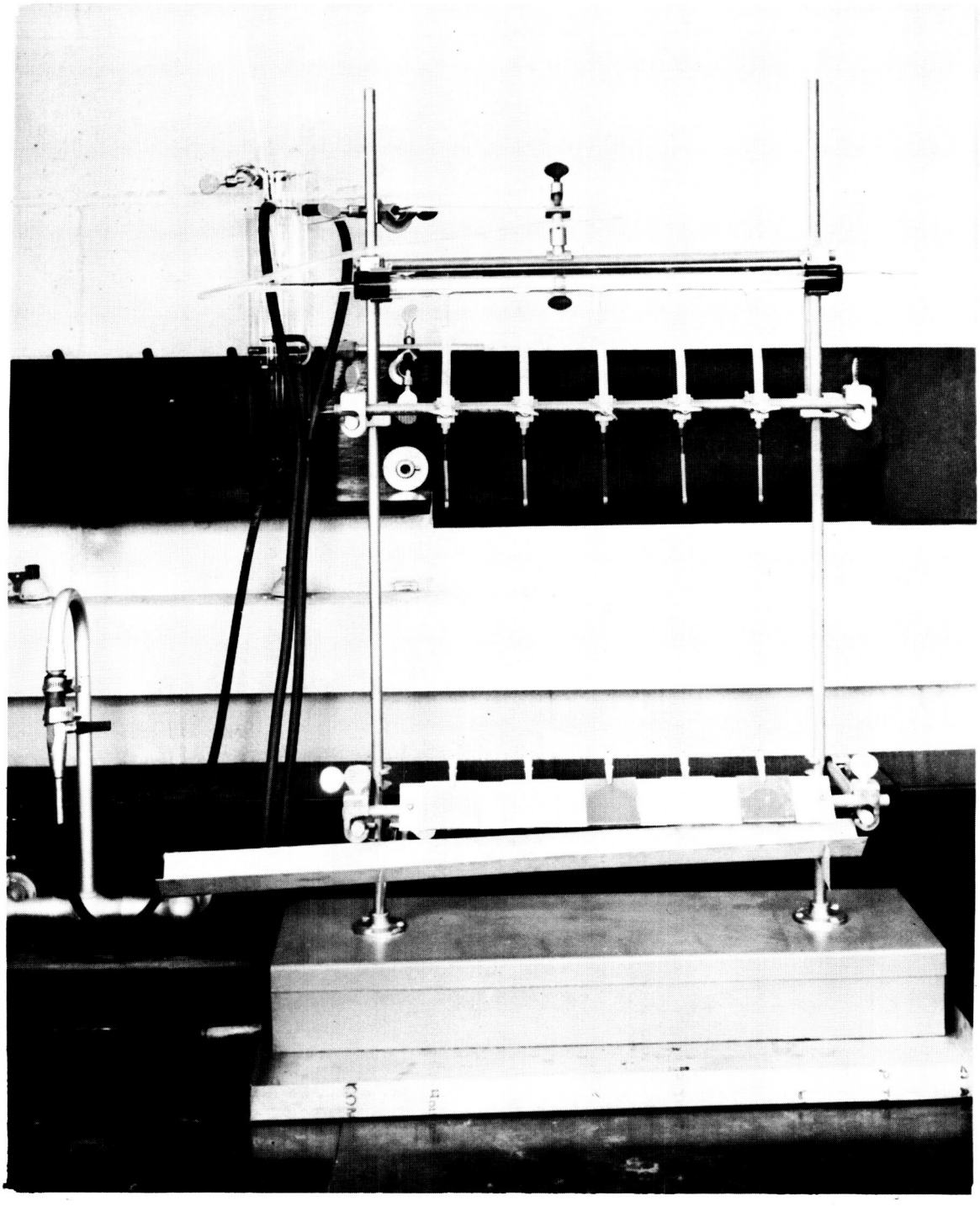


Figure 1.- Effect of curing temperature on relative hardness of four coatings bonded with monaluminum phosphate.



L-59-5045

Figure 2.- Water-dropping equipment for evaluating moisture resistance.

NACA-M

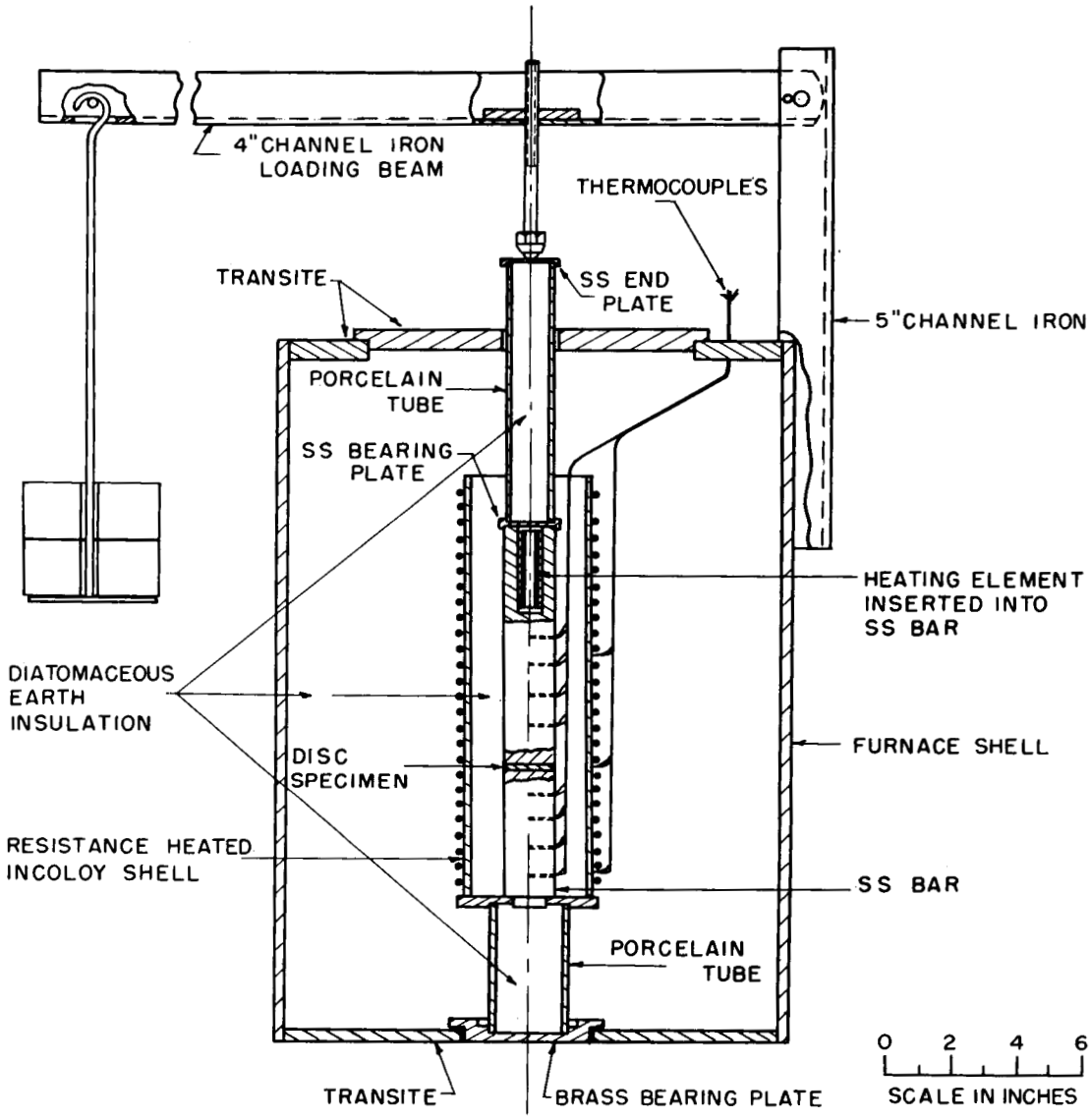


Figure 3.- Schematic drawing of apparatus used for determining thermal conductivity.

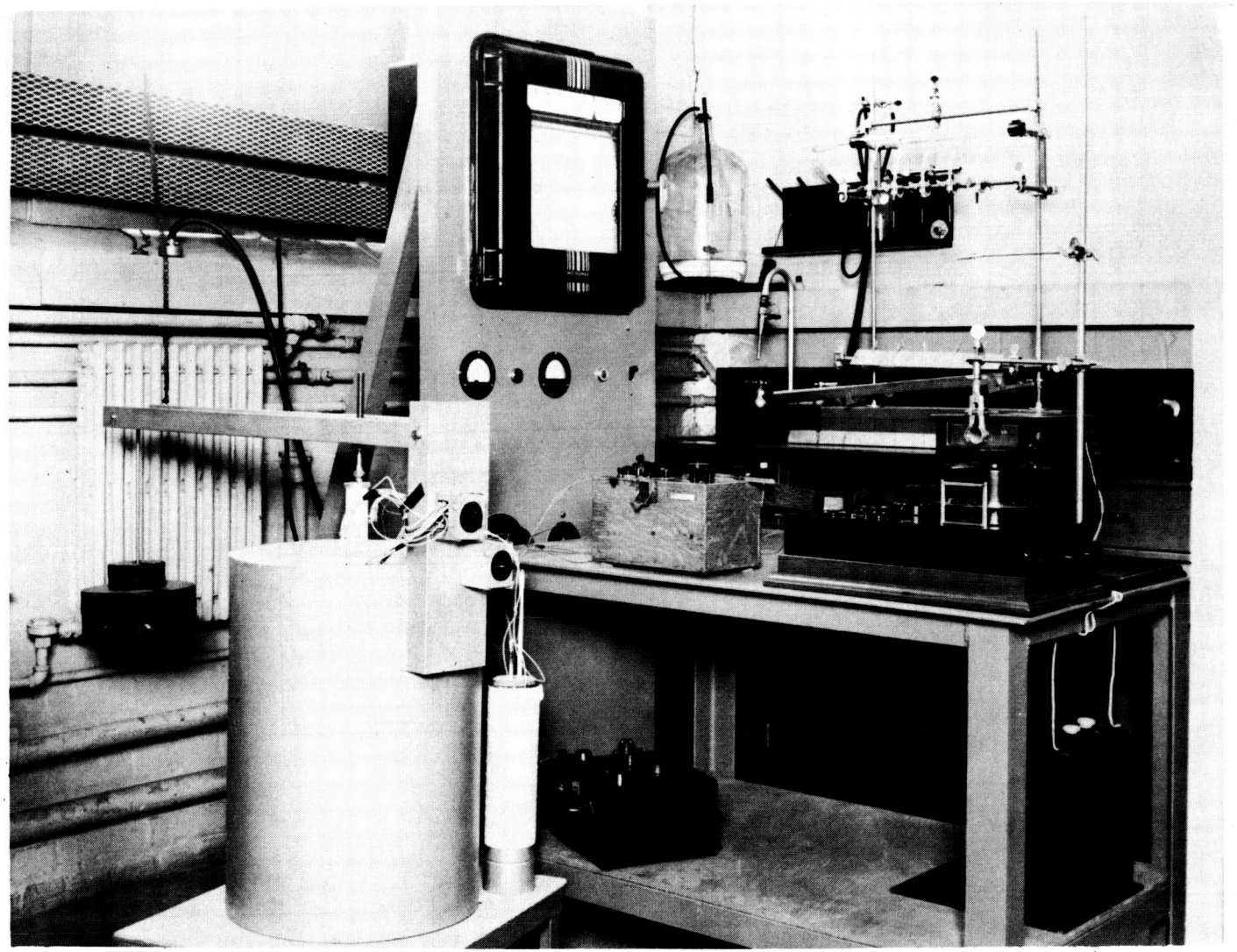


Figure 4.- Thermal-conductivity equipment. L-59-5046

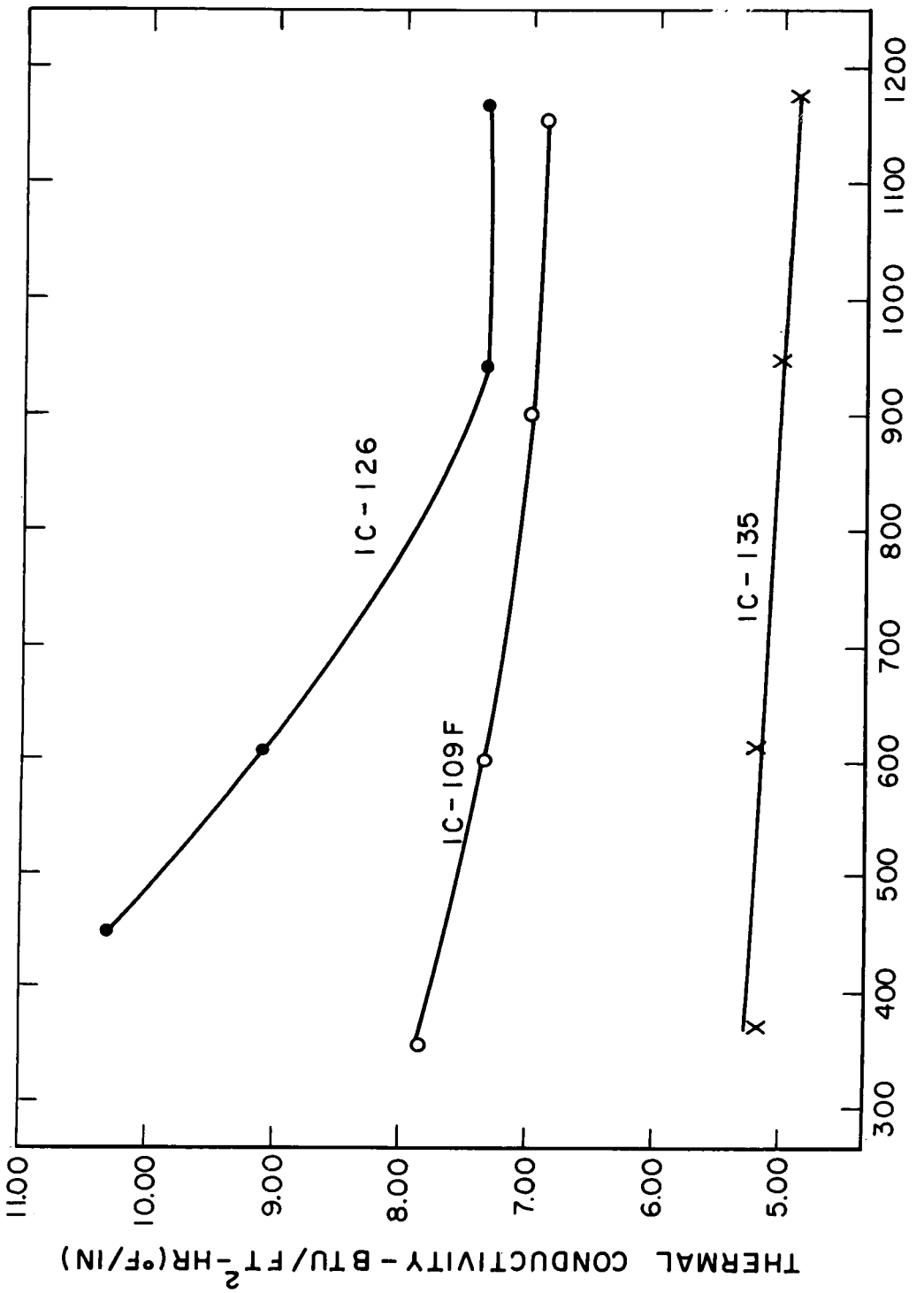


Figure 5.- Thermal conductivities of three aluminum phosphate coatings.

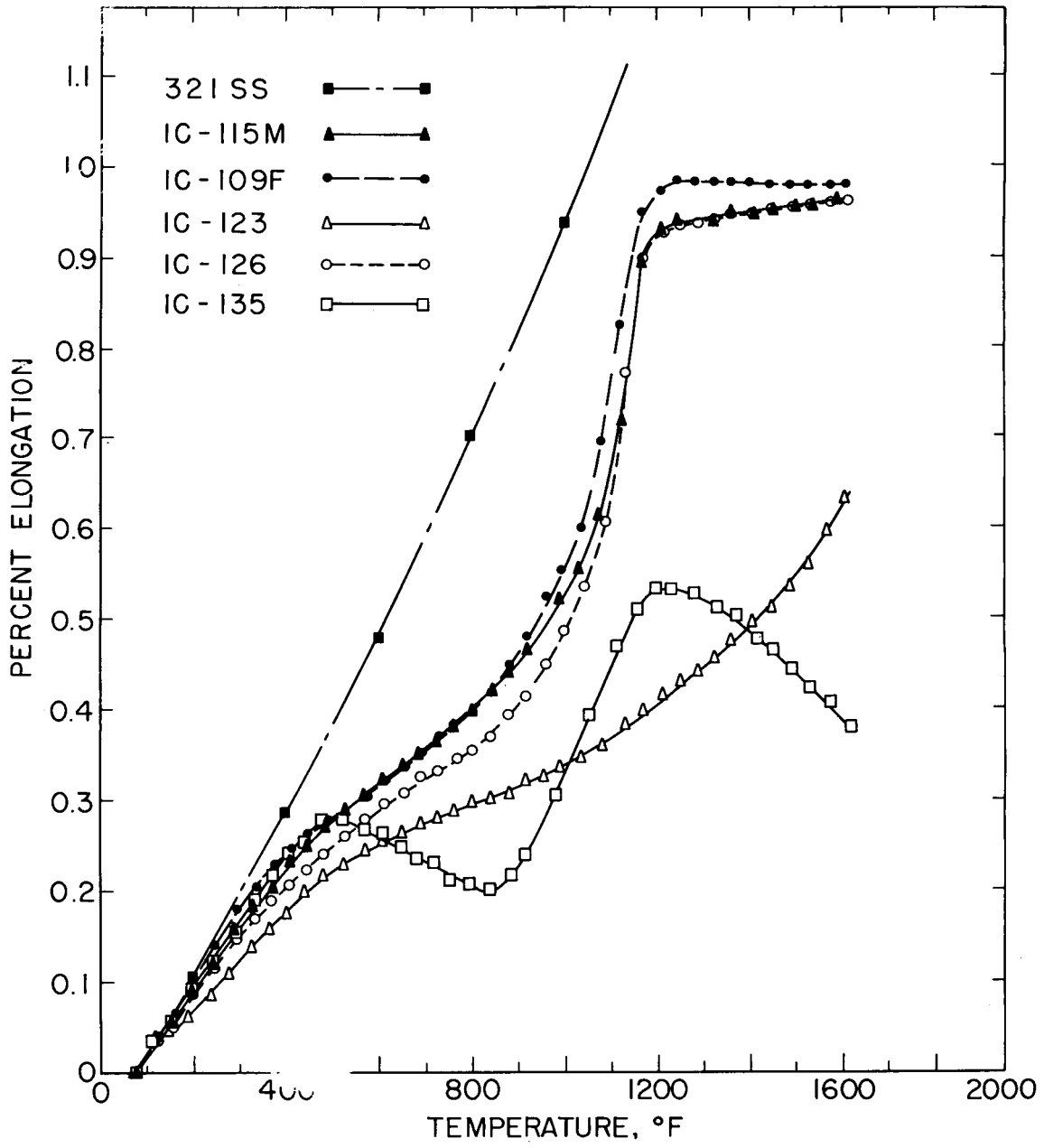


Figure 6.- Linear expansion curves of five aluminum phosphate coatings and of AISI type 321 stainless steel.

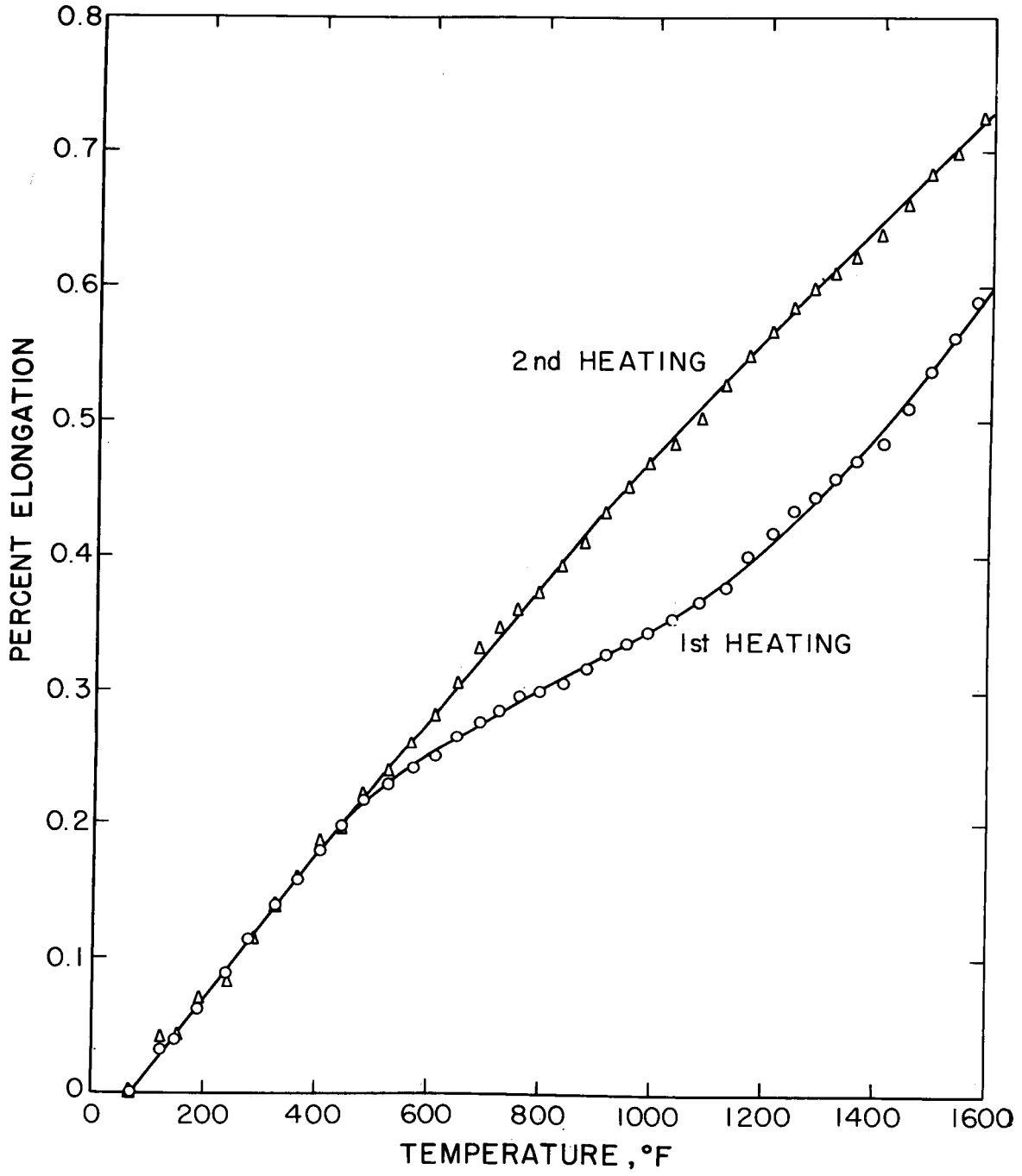


Figure 7.- Expansion curves obtained on coating IC-123 during first and second heatings.

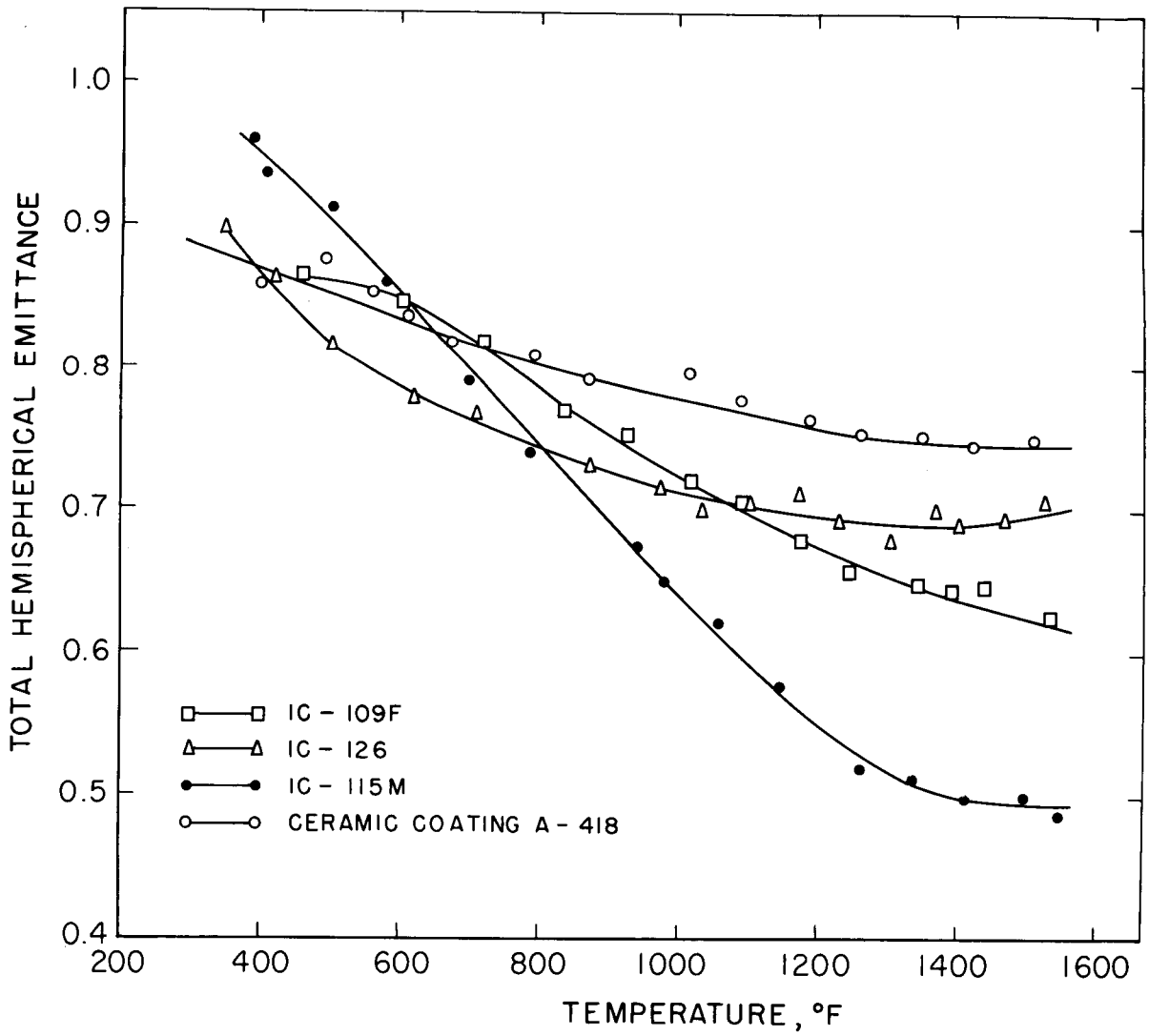


Figure 8.- Total hemispherical emittances of three aluminum phosphate coatings.